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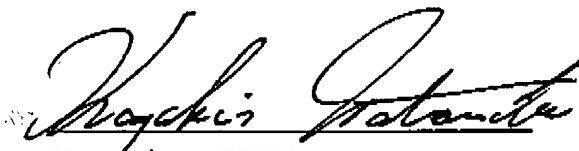
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D E C L A R A T I O N

I, Kazuhiro WATANABE, a national of Japan, c/o Sumitomo Chemical Intellectual Property Service, Limited, 5-33, Kitahama 4-chome, Chuo-ku, Osaka-shi, Osaka 541-8550, Japan, declare that to the best of my knowledge and belief the attached is a full, true and faithful translation into English made by me of the certified copy of Japanese Patent Application No. 2000-002435 attached thereto.

Signed this 30th day of May, 2003


Kazuhiro WATANABE

PATENT OFFICE
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Applicant(s) : SUMITOMO CHEMICAL COMPANY, LIMITED

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[Inventor]
[Address] c/o SUMITOMO CHEMICAL COMPANY, LIMITED,
6, Kitahara, Tsukuba-shi, Ibaraki, Japan
[Name] Kazumasa UEDA
[Inventor]
[Address] c/o SUMITOMO CHEMICAL COMPANY, LIMITED,
6, Kitahara, Tsukuba-shi, Ibaraki, Japan
[Name] Masayuki TAKASHIMA
[Applicant]
[Applicant's ID Number] 000002093
[Name] SUMITOMO CHEMICAL COMPANY, LIMITED
[Representative] Akio KOSAI
[Agent]
[Agent's ID Number] 100093285
[Patent Attorney]
[Name] Takashi KUBOYAMA
[Telephone] 06-6220-3404
[Elected Agent]
[Agent's ID Number] 100094477
[Patent Attorney]
[Name] Naoyoshi JINNO
[Telephone] 06-6220-3404
[Elected Agent]
[Agent's ID Number] 100113000
[Patent Attorney]
[Name] Toru NAKAYAMA
[Telephone] 06-6220-3404

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[Applicant]

[Applicant's ID Number] 000002093

[Address] 5-33 Kitahama 4-chome Chuo-ku Osaka-shi, Osaka

[Name] SUMITOMO CHEMICAL COMPANY, LIMITED

[Agent] Requestor

[Agent's ID Number] 100093285

[Address] c/o SUMITOMO CHEMICAL COMPANY, LIMITED,
5-33 Kitahama 4-chome Chuo-ku Osaka-shi, Osaka

[Name] Takashi KUBOYAMA

[Agent]

[Agent's ID Number] 100094477

[Address] c/o SUMITOMO CHEMICAL COMPANY, LIMITED,
5-33 Kitahama 4-chome Chuo-ku Osaka-shi, Osaka

[Name] Naoyoshi JINNO

[Agent]

[Agent's ID Number] 100113000

[Address] c/o SUMITOMO CHEMICAL COMPANY, LIMITED,
5-33 Kitahama 4-chome Chuo-ku Osaka-shi, Osaka

[Name] Toru NAKAYAMA

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Applicant's Past Record

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Address 5-33, Kitahama 4-chome, Chuo-ku, Osaka-shi,
Osaka, JAPAN

Name SUMITOMO CHEMICAL COMPANY, LIMITED

[Document name] Specification

[Title of the invention] ABRASIVE AND POLISHING COMPOSITION FOR METAL, AND PROCESSD FOR POLISHING

[Claims]

[Claim 1]

An abrasive for metal comprising a particle having a functional group capable of trapping a metal ion.

[Claim 2]

An abrasive for metal comprising a particle containing a compound having a functional group capable of trapping a metal ion.

[Claim 3]

The abrasive for metal according to claim 1 or 2, wherein the functional group capable of trapping a metal ion comprises at least one selected from the group consisting of Oxygen atom, Nitrogen atom, Sulfur atom, Phosphorus atom, Arsenic atom and Selenium atom.

[Claim 4]

The abrasive for metal according to claim 1 or 2, wherein the functional group capable of trapping a metal ion is at least one selected from the group consisting of -OH, -COOM, >C=O, -O-, -COOR, -CONH₂, -NO, -NO₂,

$\equiv N \rightarrow O$,

-SO₃M, -PHO(OM), -PO(OM)₂, -AsO(OM)₂, -NH₂, >NH,

$\equiv N$,

-N=N-, >C=N-, >C=N-OH, >C=NH, -SCN, -SH, -S-, >C=S, -COSM, -CSSM, -CSNH₂, -NCS, >P-, >As-, -SeH, >S=Se and -CSeSeM (wherein M represents hydrogen, an alkali metal, an alkaline earth metal or an ammonium group and R represents a hydrocarbon).

[Claim 5]

The abrasive for metal according to claim 2, wherein the compound having a functional group capable of trapping a metal ion is an ion exchange resin.

[Claim 6]

The abrasive for metal according to claim 2, wherein the compound having a functional group capable of trapping a metal ion is a chelate resin.

[Claim 7]

The abrasive for metal according to any one of claims 1 to 6, wherein the metal is a copper-based metal.

[Claim 8]

A polishing composition for metal comprising an abrasive for metal according to any one of claims 1 to 7, an oxidizing agent and water.

[Claim 9]

The polishing composition for metal according to claim 8, wherein the metal is a copper-based metal.

[Claim 10]

The polishing composition for metal according to claim 8 or 9, wherein the oxidizing agent is hydrogen peroxide.

[Claim 11]

A process for polishing a metal by chemical mechanical polishing, which comprises using the polishing composition for metal according to any one of claims 8 to 10 as a polishing composition.

[Claim 12]

The process for polishing according to claim 11, wherein the metal is a copper-based metal.

[Detailed description of the invention]

[0001]

[Technical field to which the invention belongs]

The present invention relates to an abrasive for polishing a metal, a polishing composition for metal, and a process for polishing using the same. More particularly, the present invention relates to a process for polishing a metal film in the production of semiconductor devices, particularly a copper-based metal film, using an abrasive, a polishing composition for metal and said polishing composition.

[0002]

[Description of the Prior art]

In recent years, various fine processing techniques have been researched and developed for advance high integration and high performance of LSI. Among them, the chemical mechanical polishing (hereinafter, abbreviated as CMP in some cases) have been attracting the attention. CMP is a composite technique

involving a chemical action and a mechanical action between a polishing composition and a material to be polished, and is an essential technique in the planarizing of insulating interlayers, particularly in the multilayer wiring formation step, in the metal plug formation, in the buried-type metal wiring formation and the like.

[0003]

From the viewpoint of speeding-up of LSI, it is considered that the main current of metals used in the metal wiring in future would be a copper-based metal with a low resistance, and formation of the buried type wiring using this copper-based metal has been recently studied actively. For the polishing of copper-based metals, compositions containing, as the main ingredients, an abrasive particle composed of a particulate inorganic oxide such as alumina or silica and an oxidizing agent such as ferric nitrate or hydrogen peroxide have previously been used generally. There has been a problem, however, that copper-based metals could not be polished with a high speed using such a polishing composition containing an abrasive of inorganic oxide and an oxidizing agent.

[0004]

For this reason, in order to improve the polishing rate of copper-based metals, a technology for high speed polishing has been developed by including of an additive with etching nature such as a complexing agent (e.g. amine and glycine etc.) capable of forming a complex with a copper ion. That is, it is a method

of polishing while etching, by reacting with a copper ion to form a water-soluble copper complex. However, in a polishing composition containing an additive with etching nature, there was a problem of occurring of dishing. That is, there has been a tendency of generating the dishing, i.e., thinning in the central portion, in wide-spread regions of metal wiring film, particularly those buried in a groove or opening, by isotropic etching of a metal when a metal wiring formed on a semiconductor substrate is polished with a polishing composition containing an additive with etching nature. When dishing occurs, problems arise that, in addition to deterioration of the planarity, high resistance as compared with a layer of buried metal wiring, and some others, will result.

[0005]

On the other hand, attempts have also been made to accomplish polishing, without etching, by polishing a copper complex, which is hardly soluble in water and more mechanically fragile than copper, formed on the surface of copper by a reaction of copper.

However, while the polishing composition forming a fragile copper complex allowed a faster polishing as compared with the above-described conventional polishing composition containing an inorganic oxide particle and an oxidizing agent, it had a problem that its polishing rate is slower than that with above-cited polishing composition with etching nature.

[0006]

In addition, copper-based metals have a low hardness, problems occurred that the surface of the copper-based metal became rough by scratches and that abrasives were embedded in the metal when particles of inorganic oxide having a high hardness were used as the abrasive.

Therefore, although a method in which a particle containing a soft organic polymer compound as the main component is used as a polishing particle has been proposed, this method had a problem that a high polishing rate could not be obtained unless it contained an additive with etching nature.

[0007]

[Problems to be solved by the invention]

The object of the present invention is to provide an abrasive for metal which allows a high speed polishing of metals, which inhibits generation of scratches on the polishing surface and which inhibits etching of the metal, a polishing composition for metal, and a process for polishing using the same.

[0008]

[Means to solve the problems]

As the result of extensive studies conducted for solving the above-described problems, the present inventors have found that the above objects can be attained by using a particle having a functional group capable of trapping a metal ion or a particle containing a compound having a functional group capable of

trapping a metal ion, and thus completed the present invention.

That is, the present invention relates to [1] an abrasive for metal comprising a particle having a functional group capable of trapping a metal ion.

Further, the present invention relates to [2] an abrasive for metal comprising a particle containing a compound having a functional group capable of trapping a metal ion.

[0009]

Also, the present invention relates to [3] a polishing composition for metal comprising the abrasive for metal described in the above [1] or [2], an oxidizing agent and water.

[0010]

Further, the present invention relates to [4] a process for polishing a metal by chemical mechanical polishing, which comprises using the polishing composition for metal described in the above [3] as a polishing composition.

[0011]

[Embodiment of the invention]

The present invention will be described below in detail.

The abrasive for metal of the present invention is characterized in that it comprises a particle having a functional group capable of trapping a metal ion.

Further, the abrasive for metal of the present invention is characterized in that it comprises a particle containing a compound having a functional group capable of trapping a metal

ion.

[0012]

The functional group capable of trapping a metal ion may be anyone that contains a coordinating atom which forms a complex with a metal, and specifically includes functional groups containing at least one selected from the group consisting of Oxygen atom, Nitrogen atom, Sulfur atom, Phosphorus atom, Arsenic atom and Selenium atom.

[0013]

Specific examples of said functional group include: -OH (compounds include alcohols, phenols or enols), -COOM (wherein M represents hydrogen, an alkali metal, an alkaline earth metal or an ammonium group, and compounds include carboxylic acids or carboxylate salts), >C=O (compounds include aldehydes, ketones or quinones), -O- (compounds include ethers), -COOR (wherein R represents a hydrocarbon group, and compounds include esters), -CONH₂ (compounds include amides), -NO (compounds include nitroso compounds), -NO₂ (compounds include nitro compounds),

$\equiv\text{N}\rightarrow\text{O}$

(compounds include N-oxides), -SO₃M (wherein M has the same meaning as defined above, and compounds include sulfonic acid or sulfonate salts), -PHO(OM) (wherein M has the same meaning as defined above, and compounds include hypophosphorous acid or hypophosphite), -PO(OM)₂ (wherein M has the same meaning as

defined above, and compounds include phosphorous acid or phosphite salts), $-\text{AsO}(\text{OM})_2$ (wherein M has the same meaning as defined above, and compounds include arsenic acid or arsonate salts), as those coordinated through an O-atom.

Specific examples of said functional group include: $-\text{NH}_2$ (compounds include primary amines), $>\text{NH}$ (compounds include secondary amines),

$\equiv\text{N}$

(compounds include tertiary amines), $-\text{N}=\text{N}-$ (compounds include azo compounds or heterocyclic compounds), $>\text{C}=\text{N}-$ (compounds include Schiff bases or heterocyclic compounds), $-\text{CONH}_2$ (compounds include amides), $>\text{C}=\text{N}-\text{OH}$ (compounds include oximes), $>\text{C}=\text{NH}$ (compounds include imines or enamines), $-\text{SCN}$ (compounds include thiocyanates), as those coordinated through a N-atom.

[0014]

Specific examples of said functional group include: $-\text{SH}$ (compounds include thioalcohols or thiophenols), $-\text{S}-$ (compounds include thioethers), $>\text{C}=\text{S}$ (compounds include thioaldehydes or thioketones), $-\text{COSM}$ (wherein M has the same meaning as defined above, and compounds include thiocarboxylic acids or thiocarboxylate salts), $-\text{CSSM}$ (wherein M has the same meaning as defined above, and compounds include dithiocarboxylic acids or dithiocarboxylate salts), $-\text{CSNH}_2$ (compounds include thioamides), $-\text{NCS}$ (compounds include isothiocyanates), as those coordinated through a S-atom.

[0015]

Specific examples of said functional group include : $>P-$ (compounds include primary, secondary or tertiary alkyl or aryl phosphine), as those coordinated thorough a P-atom.

Specific examples of said functional group include : $>As-$ (compounds include primary, secondary or tertiary alkyl or aryl arsene), as those coordinated through an As-atom.

Specific examples of said functional group include : $-SeH$ (compounds include selenols), $>C=Se$ (compounds include selenocarbonyl compounds) and $-CSeSeM$ (wherein M has the same meaning as defined above, and compounds include diselenocarboxylic acids or diselenocarboxylate salts), as those coordinated through a Se-atom.

[0016]

Among these functional groups capable of trapping a metal ion, preferred are $-OH$, $-COOM$, $>C=O$, $-O-$, $-SO_3M$, $-PO(OM)_2$, $-NH_2$, $>NH$,

 $\equiv N$,

$-SH$, $-S-$, $-COSM$ and $-CSSM$ (M has the same meaning as defined above).

[0017]

These functional groups may be used alone or in combination of two or more. When two or more functional groups are used in combination, particles having different functional groups or particles containing compounds having different functional

groups may be used, and a particle having two or more functional groups or a particle containing a compound having two or more functional groups may be used. Examples of the particle having two or more functional groups or the particle containing a compound having two or more functional groups include those having aminocarboxylic acids, aminoalcohols, aminophosphonic acids and the like as the functional group.

[0018]

The functional group capable of trapping a metal ion desirably exists on the surface of the particle. Even if the group does not exist on the surface of the particle, the same effect can be obtained when the functional group capable of trapping a metal ion can appear on the surface of the particle and can contact with a metal to be polished by crushing of the particle due to stress on polishing, by peeling of a coating film or by other situations.

[0019]

As the particle having a functional group capable of trapping a metal ion, there can be used particles of a metal oxide such as alumina, titania, zirconia, silica, ceria and the like to which said functional group is introduced. Introduction of the functional group can be performed by applying the known method. For example, in the case of a particle of a metal oxide, a usable particle can be obtained by reacting a silane coupling agent or titanate coupling agent having the desired functional

group, as the particle containing a compound having a functional group capable of trapping a metal ion, with particles of a metal oxide.

[0020]

In addition, polymer particles having the functional group introduced therein can be used as the particle having a functional group capable of trapping a metal ion. Introduction of the functional group can be performed by applying the known method. For example, in the case of a polymer particle, a usable particle can be obtained by a method in which a monomer having the desired functional group is polymerized, by a method in which any other functional group in a polymerized polymer particle is chemically converted into the desired functional group or by other methods. Polymer particles are preferred because generation of scratches during polishing can be inhibited due to their soft nature as compared with particles of metal oxide.

[0021]

Specific examples of the polymer particle having a functional group capable of trapping a metal ion include a particle of an ion exchange resin. Said ion exchange resin includes cation exchange resins, anion exchange resins and chelate resins. Examples of the cation exchange resins include cation exchange resins having $-SO_3M$ (wherein M has the same meaning as defined above, and compounds include sulfonic acids or sulfonate salts), $-COOM$ (wherein M has the same meaning as

defined above, and compounds include carboxylic acids or carboxylate salts) or the like as the functional group. Examples of the anion exchange resins include anion exchange resins having an amino group, a mono-substituted amino group, a di-substituted amino group or the like as the functional group. Examples of the chelate resins include chelate resins having an aminocarboxylic acid, an aminophosphonic acid, an iminodiacetic acid or the like as the functional group.

[0022]

The chelate resins are resins having, on their surface, a multi-dentate ligand which has plural coordinating atoms forming a complex with a metal. In general, when a multi-dentate ligand having two or more coordinating atoms is bound to a metal ion, a chelate ring is formed resulting in a greater stability than a complex coordinated with a mono-dentate ligand. Such case is preferred because the capacity of trapping an ion of a metal to be polished becomes greater.

[0023]

In addition, a particle containing a compound having a functional group capable of trapping a metal ion includes metal oxide particles and polymer particles containing a compound having the functional group. Specifically, the particle can be obtained by impregnating or covering metal oxide particles or polymer particles with the compound,.

[0024]

Next, the polishing composition of the present invention is characterized in that it comprises the particle having a functional group capable of trapping a metal ion or the particle containing a compound having a functional group capable of trapping a metal ion, an oxidizing agent and water.

The oxidizing agent used in the polishing composition for metal of the present invention has preferably an effect of improving the polishing rate. Although the polishing mechanism is not clear, it can be contemplated that, by promoting a reaction of oxidizing a metal to be polished, a complex forming reaction between a metal and a functional group capable of trapping a metal ion is promoted and, thus, the polishing rate is improved. As the oxidizing agent, the known oxidizing agents can be applied. Examples of the oxidizing agent include hydrogen peroxide, iodic acid, iodate and the like, with hydrogen peroxide being recommended to be applied.

[0025]

The usual concentration of the oxidizing agent in the polishing composition is desirably within a range of about 0.1 to 15% by weight based on said polishing composition. When the concentration of said oxidizing agent is lower than 0.1% by weight, it is difficult to exhibit the effect of improving the polishing rate. On the other hand, when the concentration exceeds 15 % by weight, it is uneconomical because the polishing rate may not be improved in proportion to the concentration.

In addition, the time of adding said oxidizing agent is not particularly limited insofar as the oxidizing agent is not deteriorated. Addition immediately before the polishing is recommended because sometimes its effect is lowered by the change of quality with time.

[0026]

When said abrasive is used for polishing a metal, it is used in the form of a slurry-form polishing composition in which said abrasive and oxidizing agent are dispersed in water. Formation of the polishing composition can be accomplished by simultaneously mixing and dispersing an abrasive, an oxidizing agent and water, or by previously mixing an abrasive and water, an abrasive and an oxidizing agent, or an oxidizing agent and water, and then mixing and dispersing with other ingredients missing therein for use in polishing in the form of a polishing composition. The dispersing method for forming a slurry can be a known method, including methods using a homogenizer, ultrasonic wave, wet mill and the like. The concentration of the slurry (the content of the abrasive in the polishing composition) may usually be about 1 to 30% by weight.

[0027]

The polishing composition of the present invention may contain, if necessary, an additive such as a surfactant for the purpose of improving the stability of dispersion, inhibition of sedimentation, roughness of polishing surface and the like.

The surfactant may be anionic, cationic, nonionic or amphoteric, and two or more of them can be used in combination.

[0028]

While the pH of the polishing composition of the present invention is not critical because pH effective for polishing depends on the kind of the functional group or the kind of metal to be treated, a usual value is about 1 to 8 and preferably 2 to 6. When the pH of the polishing composition is lower than 1, a problem about the handling of the polishing composition or corrosion of polishing apparatus may arise. The pH of the polishing composition of the present invention can be adjusted with a known acid or alkali. It is desirable to use an acid or alkali free of metal ion such as nitric acid, phosphoric acid, sulfuric acid, ammonium hydroxide, amine or the like.

[0029]

The polishing composition of the present invention can be used for polishing various metals, suitably copper-based metal. Said polishing composition is preferably used for polishing metal films, particularly copper-based metal films formed on semiconductor substrates. The copper-based metal includes pure copper film, copper alloy film and the like.

[0030]

By using the polishing composition of the present invention, metals can be polished at a high speed, and generation of scratches on the polishing surface and as well as etching of the metal

can be inhibited.

[0031]

That is, when a particle having a functional group capable of trapping a metal ion is used as an abrasive, the same polishing promoting effect as that of an additive with etching nature can be obtained by forming a complex by the functional group and a metal to be polished. However, since the functional group is present in a solid particle, and a complex produced by a reaction with a metal is trapped by a polishing particle and, thus, it does not become a water-soluble complex, etching does not occur. In addition, since the above-mentioned reaction occurs only at a part where an abrasive and a metal are contacted, polishing progresses preferentially at a convex part, and a flat polished surface can be obtained.

[0032]

Next, the process for polishing according to the present invention is a process for polishing a metal by chemical mechanical polishing and characterized by use of the above-described polishing composition for metal of the present invention as the polishing composition. The process for polishing according to the present invention can be preferably applied to metal films, particularly metal films formed on semiconductor substrates.

[0033]

[Examples]

The present invention will be described below with reference to Examples, but the present invention is not limited by them.

Example 1

(Preparation of a polishing composition)

A chelate resin having an aminocarboxylic acid group as a functional group capable of trapping a metal ion (trade name: Sumichelate MC-75, manufactured by Sumitomo Chemical Co., Ltd.) was subjected to wet-dispersing using a ball mill. Hydrogen peroxide as an oxidizing agent was added to the obtained slurry, the mixture was adjusted to an abrasive concentration of 2.5% by weight and a hydrogen peroxide concentration of 1.5% by weight and then pH was adjusted to 5 or 3 with nitric acid to give a polishing composition.

[0034]

(Polishing of a copper film)

Using the above polishing composition, a wafer having a copper film formed by sputtering was polished with a polishing machine (MECAPOL E-460, manufactured by PRESI). The polishing conditions included a revolution number of rotary platen of 60 rpm, a revolution number of a holding jig for wafer of 60 rpm, a polishing pressure of 200g/cm², a flow rate of polishing composition of 100 ml/minute and polishing period of 30 seconds. The results of polishing are shown in Table 1.

[0035]

Example 2

A chelate resin having an iminodiacetic acid group as a functional group capable of trapping a metal ion (trade name : Sumichelate MC-700, manufactured by Sumitomo Chemical Co., Ltd.) was subjected to wet-dispersing using a ball mill. Hydrogen peroxide as an oxidizing agent was added to the obtained slurry, the mixture was adjusted to an abrasive concentration of 2.5% by weight and a hydrogen peroxide concentration of 1.5% by weight and then pH was adjusted to 5 or 3 with nitric acid to give a polishing composition. Copper films were polished in the same manner as in Example 1. The results are shown in Table 1.

[0036]

Example 3

An ion exchange resin having a carboxylic acid group as a functional group capable of trapping a metal ion (trade name : Duolite C 476, manufactured by Rhom & Haas Co.) was subjected to wet-dispersing using a ball mill. Hydrogen peroxide as an oxidizing agent was added to the obtained slurry, the mixture was adjusted to an abrasive concentration of 2.5% by weight and a hydrogen peroxide concentration of 1.5% by weight and then pH was adjusted to 3 with nitric acid to give a polishing composition. A copper film was polished in the same manner as in Example 1. The result is shown in Table 1.

[0037]

Comparative Example 1

Colloidal silica (trade name : Snowtex, manufactured by Nissan Chemical Ind.), a particle of inorganic oxide, was used as the abrasive for polishing. The abrasive concentration was adjusted to 2.5% by weight and the hydrogen peroxide concentration was adjusted to 1.5% by weight and then pH was adjusted to 5 or 3 with nitric acid to give a polishing composition. Copper films were polished in the same manner as in Example 1. The results are shown in Table 1.

[0038]

Comparative Example 2

PMMA aqueous emulsion resin was used as the abrasive for polishing. The abrasive concentration was adjusted to 2.5% by weight and the hydrogen peroxide concentration was adjusted to 1.5% by weight and then pH was adjusted to 3 with potassium hydroxide to give a polishing composition. A copper film was polished in the same manner as in Example 1. The result is shown in Table 1.

[0039]

[Table 1]

	PH	Polishing rate (Å/min)
Example 1	5	828
	3	1620
Example 2	5	661
	3	4956
Example 3	3	2818
Comparative Example 1	5	376
	3	547
Comparative Example 2	3	362

[0040]

In the cases of Examples 1 to 3 using the polishing compositions comprising a particle having a functional group capable of trapping a metal ion, a high polishing rate is obtained. However, in the cases of Comparative Example 1 using the polishing composition comprising colloidal silica and Comparative Example 2 using the polishing composition comprising PMMA aqueous emulsion resin, the polishing rate was slow.

[0041]

[Effects of the invention]

Since use of the abrasive for metal, the composition for metal polishing and the process for polishing a metal using them enables a high speed polishing of metals, particularly metal films, inhibition of generation of scratches on the polishing surface and inhibition of etching of the metal, the present invention has a great industrial value.

[Document name] Abstract

[Abstract]

[Object] To provide an abrasive for metal and a polishing composition for metal, which allow a high speed polishing of metals, which inhibit generation of scratches on the polishing surface and which inhibit etching of the metal, and a process for polishing using the same.

[Solving means]

[1] An abrasive for metal comprising a particle having a functional group capable of trapping a metal ion.

[2] A polishing composition for metal comprising the abrasive for metal described in the above [1], an oxidizing agent and water.

[3] A process for polishing a metal by chemical mechanical polishing, which comprises using the polishing composition for metal described in the above [2] as a polishing composition.

[Selected drawing] None